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| <b>(21) International Application Number:</b> PCT/EP99/01974<br><b>(22) International Filing Date:</b> 23 March 1999 (23.03.99)<br><b>(30) Priority Data:</b><br>98201179.3 14 April 1998 (14.04.98) EP<br><b>(71) Applicant (for all designated States except AE AU BB CA GB IE IL KE LK LS MW NZ SD SG SZ TT UG ZA):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).<br><b>(71) Applicant (for AE AU BB CA GB IE IL KE LK LS MW NZ SD SG SZ TT UG ZA only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).<br><b>(72) Inventors:</b> VAN BUUREN, Jan; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). VAN PUTTE, Karel, P., A., M.; Unilever Research Vlaardingen, Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL).<br><b>(74) Agent:</b> SIKKEN, Antonius; Patent Dept., Olivier van Noortlaan 120, NL-3133 AT Vlaardingen (NL). |           | <b>(81) Designated States:</b> AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).<br><br><b>Published</b><br><i>With international search report.</i><br><i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i> |
| <b>(54) Title:</b> FORTIFICATION OF A VEGETABLE FAT WITH ANTIOXIDANTS<br><b>(57) Abstract</b><br><p>For at least one day olive fruits are soaked in vegetable oil, preferably in olive oil, with the effect that polyphenols diffuse into the surrounding oil. The raise of polyphenols in this oil is at least 10 ppm. The migrating polyphenols typically are fat soluble polyphenols. Treated oils show an increased stability to oxidation. Their flavour has improved and often receives a higher appreciation than the flavour of the starting oil.</p>  |           |  |

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## FORTIFICATION OF A VEGETABLE FAT WITH ANTIOXIDANTS

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The present invention deals with vegetable oils and with a method to increase the level of anti-oxidants, particularly of olive polyphenols.

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### BACKGROUND OF THE INVENTION

The present invention deals with vegetable fats and oils,  
10 particularly with olive oil. Fats and oils form a  
substantial part of the average human food consumption.  
Since fat consumption is associated with an increased risk  
of cardiovascular disorders, the nutritional value of  
different types of fat as well as methods for reducing the  
15 amount of fat in food compositions had been the object of  
extensive investigations. Presently not only the  
triglyceride part of fats is the subject of such  
investigations, but also the nature and the effects on  
health of fat attributes, the so-called minor components  
20 which are present in small amounts in non-refined natural  
fats. It has recently been found that the minor components  
which are denoted as anti-oxidants, including fat

polyphenols, positively interfere with the body's cardiovascular system.

Traditionally, most natural fats are refined before they are used as an ingredient for the preparation of food.

5 However, traditional fat refining is not discriminating to the nature of the fat ingredients and aims at the removal of all substances other than triglycerides, including minor components.

10 Oils and fats aimed for human consumption are subjected to a refining treatment. Only for a minor part of those the refining is limited to a simple water washing and decantation or centrifugation. Such so-called virgin oils, particularly virgin olive oils, are much appreciated for  
15 their rich taste.

Most fats and oils, however, are purified and deodorised by a refining treatment under, often, drastic conditions.

Impure olive oil e.g., traditionally is deodorized at

20 temperatures of 250°C or even more. Under such conditions also the oil's valuable minor components, including natural anti-oxidants, particularly the typical olive oil polyphenols are nearly fully stripped away.

25 WO 97/06697 teaches that food products can be fortified with anti-oxidants, including polyphenols. The patent particularly discloses the use of water soluble tea polyphenols.

Polyphenols present in olive oil are more or less fat  
30 soluble and have a chemical composition different from the water soluble polyphenols. They are presumed to play in the body an anti-oxidant role in specific tissues, possibly because of their fat solubility.

35 The introduction or re-introduction of polyphenols in refined vegetable oils, including olive oil, in a simple,

natural and cheap way is the subject of the present invention.

5

#### SUMMARY OF THE INVENTION

We have found a method for fortification of vegetable oils with any ingredient of olive fruits, characterized in that olive fruits together with a vegetable oil are stored in a  
10 container of at least 5 liters, are allowed to soak in the oil for at least one day and finally are separated from the oil.

15

#### DETAILS OF THE INVENTION

The method is of utmost simplicity but with a quite beneficial effect. The treated oil shows a significant increase of useful minor components, particularly of  
20 polyphenols.

The method can be used for all types of vegetable oils such as rapeseed oil, corn oil, sunflower seed oil, soybean oil but olive oil is preferred. The oils may be refined or non-  
25 refined.

The invention is not limited to fortification of oils which are devoid of any polyphenol, either by nature or because of a refining process, but also of oils which contain  
30 polyphenols of their own such as virgin olive oils.

A raise of 10 ppm or more of polyphenols content is a significant increase. Usually polyphenols are present not as a single compound but as a mixture of different  
35 polyphenols.

Polyphenols are compounds which share a phenolic hydroxyl

## 4.

group. The main olive oil originating polyphenols comprise oleuropein, aglycon, tyrosol and hydroxytyrosol.

The total content of polyphenols in olive oils can be  
5 established by standard methods e.g. by the colorimetric  
Gutfinger method as described in J.Am.Oil.Chem.Soc. 1981,  
11, pp. 966-968, which method is based on the reaction of a  
methanolic extract of olive oil and the Folin-Ciocalteau  
reagent. This method has been used for establishing the  
10 polyphenol values mentioned in the present patent  
specification.

The effect of the described process can be increased  
further when the olive fruits are first subjected to a  
15 treatment which enhances the transport of the olive fruit  
ingredients from the fruit into the oil.

Such treatment comprises crushing, freezing and thawing,  
sonication, heat shock, drying and high pressure shock.

Excluded are treatments which cause the disintegration of  
20 the olive fruits so that particles are formed.

A further measure to enhance the fortification effect is to  
select the harvest time of the olive fruits such that they  
have matured to their maximum polyphenols content, usually  
25 in the begin phase of their ripening. The olives should not  
be debittered since this causes a decrease of the  
polyphenols content. Usually GREEN olives give the best  
results.

30 Another aspect of the invention is the use of the fortified  
oils for the preparation of food compositions in which a  
vegetable oil is an ingredient. Such food compositions  
become enriched as well with the valuable polyphenols.

35 Such compositions may be spreads, as exemplified in our co-

pending patent application PCT/EP 98/07797, but also food compositions other than spreads which are characterized by the presence of 5 - 100 wt.% of a vegetable oil, as are mayonnaises, dressings, tomato sauces and salad oils. The food compositions of the present invention contain at least 10 ppm, preferably at least 50 ppm, more preferably at least 200 ppm of olive oil originating polyphenols.

Processes for the manufacture of these compositions are well known in the art and need no illustration. Such compositions form part of the invention when at least a part of the usual oil ingredient have been substituted by the vegetable oil prepared according to the present invention.

Oils obtained according to the invention are further characterized by a specific partition of the various types of olive oil polyphenols, caused by the invented method of exporting polyphenols from their olive source to an oil destination. The polyphenols migration principally follow the dynamics of diffusion processes and the partition rules between fat phase (as present in oil and in olive) and aqueous phase (olive). The distribution of the various polyphenols over the phases is mainly dependent on the lipophilic/hydrophilic balance of each individual polyphenol.

The method of the invention uses a relatively slow diffusion process which requires an exposure time of at least one day, preferably at least two days, more preferably at least one week. An upper time limit does not exist, but flavour assessments have provided indications that flavour quality has a tendency to decline after thirty days. Therefore the fortification process is finalized by separation of the olives, preferably, after thirty days.

Various properties of the oil are changed by the increased polyphenols content. The oxidation stability of the oil is improved proportional to the increase of the polyphenols level.

5

A further surprising and beneficial effect which results from the present invention is the remarkable flavour improvement of a non-refined olive oil when treated according to the invention. See example 1.

10 Possibly, such impact on oil flavour could be ascribed, at least partially, to some absorption of off-flavour components to the fruit body of the olive.

Said flavour improvement can be established not only by an  
15 organoleptic assessment, but also by a measurable shift in the volatiles/non-volatiles balance. The volatiles are arbitrarily defined as the components of olive oil having a boiling point of at least 175°C, while all higher boiling components are denoted as non-volatiles. It is an  
20 established fact that the appreciation of olive oil flavour is proportional to the ratio of total amounts of volatiles and non-volatiles, which is the volatiles/non-volatiles balance.

During soaking of the olives in the olive oil the ratio of  
25 the balance increases during the first fortnight. After the next fortnight the increase is less.

This effect depends on the type of olives. No ratio increase was found when green, debittered olives were used.

30 The invention is not restricted to oils which have a vegetable origin. The use of a fat blend which partly consists of vegetable fat and partly of animal fat and/or marine oils and/or fats derived from such fats/oils by fractionation or interesterification, might be  
35 advantageous.



Fat and oil are terms used in this specification interchangeably. The term oil is rather used when the fat at ambient temperature is liquid. Since the soaking with olive fruits is carried out usually at or close to ambient temperature (20°-25°C) the fat should have a liquid consistency.

Jars and bottles filled with at least olive oil and olives, often supplemented with some herbs are sold as retail products with a fancy appearance. These products have nothing to do with the industrial fortification process as described in the present specification. Said industrial processes are carried out on a large scale employing vessels having a content of at least 5 liter, preferably at least 20 liter, more preferably at least 50 liter, even more preferably at least 100 liter.

The invention is illustrated by the following examples:

#### Example 1

#### POLYPHENOLS FORTIFICATION

TABLE I

| Olive oil                                      | POLYPHENOLS CONTENT (ppm) |                |
|--|---------------------------|----------------|
|  | Paranzane olives          | Leccino olives |
| Untreated Toscane virgin olive oil             | 270                       | 420            |
| when soaked 30 days with non-debittered olives | 337                       | 591            |

Toscane non-debittered olives (10 wt.%) were slowly stirred with Toscane extra virgin olive oil during 30 days.

5 The increase of polyphenols in the olive oil is shown in Table I

### Example 2

10

### POLYPHENOLS FORTIFICATION

Italian non-debittered olives (25 wt.% of Castel olives on oil) were slowly stirred with French PUGET extra virgin olive oil during only one day. The polyphenols content was  
15 measured before and after soaking. The treatment was repeated but with 25 wt.% of Grevepesa olives.

The increase of polyphenols in the olive oil is shown in Table II.

20

TABLE II

| Olive oil                              | POLYPHENOLS CONTENT (ppm) |                  |
|--|---------------------------|------------------|
|  | Castel olives             | Grevepesa olives |
| Untreated French virgin olive oil      | 169                       | 169              |
| when soaked with non-debittered olives | 180                       | 205              |

**Exempl 3****FLAVOUR ASSESSMENT**

5 1 l of Toscane extra virgin olive oil was stirred for 26 days in the dark at 25°C with 100 g of black, intact, debittered olives from Turkey. The olive oil surface was protected by a layer of nitrogen gas. A parallel experiment was carried out but using green olives.

10

**TABLE III**

|                                   | <b>FLAVOUR ASSESSMENT</b>                          |  |
|-----------------------------------|--|--|
| <b>Sample contact time (days)</b> | <b>Black olives with olive oil</b>                 | <b>Green olives with olive oil</b>           |
| 0                                 | little bit fruity, no strong taste                 | little bit fruity, no strong taste           |
| 2                                 | clearly perceptible shift of taste                 | little bit flat taste                        |
| 5                                 | new taste has intensified                          | sweet and mild taste                         |
| 9                                 | taste identical to the olive fruits, no aftertaste | mild and a little aftertaste                 |
| 14                                | taste has further intensified                      | taste becomes flatter aftertaste perceptible |
| 26                                | still stronger black olives taste, no aftertaste   | taste defective aftertaste                   |

After specific time intervals samples were subjected to a flavour assessment (Table III) and also the ratio of volatiles and non-volatiles was established (Table IV).

5

TABLE IV

|                                  | RATIO VOLATILES / NON-VOLATILES |                                |
|----------------------------------|---------------------------------|--------------------------------|
| Sample<br>contact time<br>(days) | Black olives<br>with olive oil  | Green olives<br>with olive oil |
| 0                                | 2.8                             | 2.8                            |
| 14                               | 3.7                             | 0.5                            |
| 26                               | 1.4                             | 0.2                            |

## CLAIMS

1. Method for fortification of a vegetable fat with any ingredient of olive fruits, characterized in that olive fruits together with a vegetable oil
  - are stored in a container of at least 5 liters,
  - are allowed to soak in the oil for at least one day,
  - are finally separated from the oil.
2. Method according to claim 1, characterized in that the vegetable fat is olive oil.
3. Method according to claim 1, characterized in that the ingredient is a polyphenol or a mixture of polyphenols.
4. Method according to claim 1, characterized in that the fortification results in an increase of the polyphenols content with at least 10 ppm.
5. Method according to claim 1, characterized in that the olive fruits have been subjected to a treatment which enhances transport of the desired olive ingredient from the olive into the oil.
6. Method according to claim 5, characterized in that the treatment is chosen from crushing, freezing and thawing, sonication, drying, heat shock and high pressure shock.
7. Method according to claim 1, characterized in that olives are chosen which have been harvested in the month when the olives have their maximum polyphenols content.
8. Method according to claim 1, characterized in that the container has a volume of at least 20 liters, preferably at least 50 liters, more preferably at least 100 liters.

9. Vegetable oil fortified according to claim 1.

10. Food composition prepared with an oil according to the previous claim.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 99/01974

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 A23D9/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A23D A23L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category * | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
|------------|---|-----------------------|
| A          | FR 2 192 566 A (CHARIER VADROT IERRE)<br>8 February 1974 (1974-02-08)<br>claims 1,10  | 1,9                   |
| A          | PATENT ABSTRACTS OF JAPAN<br>vol. 009, no. 078 (C-274),<br>6 April 1985 (1985-04-06),<br>-& JP 59 213368 A (HANAMARUKI KK),<br>3 December 1984 (1984-12-03)<br>abstract                     | 1,9,10                |
| A          | WO 97 06697 A (UNILEVER NV ;UNILEVER PLC<br>(GB)) 27 February 1997 (1997-02-27)<br>cited in the application<br>page 4, line 26 - line 30<br>page 6, line 25 - page 7, line 2<br>claims 1-10 | 1,9,10                |

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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| C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT |   |                       |
|--|---|-----------------------|
| Category *   | Citation of document, with indication, where appropriate, of the relevant passages  | Relevant to claim No. |
| A  | WO 97 32947 A (COMITER TRADING & SERVICES<br>S R ;BALDI ALESSANDRO (IT); ROMANI ANNA)<br>12 September 1997 (1997-09-12)<br>claims 1,10,20<br>---- | 1,9,10                |
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

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PCT/EP 99/01974

| Patent document<br>cited in search report |   | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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